

Influence of technological parameters on the vanadium valence form in slags

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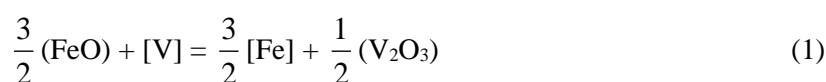
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Abstract. The multivalence of vanadium in oxide melts is considered. It is shown that the vanadium oxidation state in the slags is determined by the slag and metal compositions as well as the oxidation potential of the gas phase. Using a polymer model, vanadium valence form fractions were calculated depending on technological parameters. Calculations show that in an air atmosphere, vanadium in the slag should be predominantly in the tetravalent and trivalent state, and in contact with the molten iron, mainly in the trivalent and partly divalent state. Upon contact with pig iron, VO oxide becomes the main form of vanadium in the slag. Slag basicity and temperature have a significant effect on the relationship of vanadium forms. The suggested design-basis using the polymer model can be useful in accomplishment of the thermodynamic calculations for the vanadium equilibrium distribution between metal and slag in the iron and steel production. It allows us to describe the dependence of the vanadium oxidation state on the free oxygen activity in the slag and the gas phase oxidation potential.

1. Introduction

Thermodynamic calculations of the vanadium distribution between the metal and slag are complicated by the vanadium multivalence, as it can be present in oxide melts in two-, three-, four- and pentavalent forms. In addition, the vanadium valency determines not only the equilibrium distribution, but also the kinetics of its transition between phases. Information on vanadium-containing oxide melts is mainly based on the results of bulk, petrographic and phase analysis of solidified slags. The slag composition effect on the form of vanadium existence is obvious.

Various experimental data are presented on the effect of the blast furnace and steelmaking slag composition and, in particular, their basicity ($B = \%CaO : \%SiO_2$) on the vanadium distribution coefficient between oxide and iron-based metal melts. For slags formed during the vanadium pig iron production [1], this coefficient decreases with an increase in the basicity of the oxide melt, while the opposite effect is observed for ferrous steel-making slags [2]. A weak dependence of the vanadium oxides activity on the basicity of slag is observed in the low-alloyed vanadium steels production in electric arc furnaces [3]. The relationship between the distribution coefficient of vanadium and the iron oxides content in the slag during the smelting of low alloy steel in industrial units is clearly manifested [4, 5]. The data presented indicate the trivalent vanadium state in the slag and the decisive role in its distribution of the reaction



According to [5, 6], the value of the vanadium trioxide activity coefficient $\gamma_{V_2O_3}$ in acid, neutral and basic steelmaking slags when normalized to pure solid vanadium trioxide is 2.6–2.8, which indicates the invariance of the valence state and a limited V_2O_3 solubility in the studied systems. However, the



data represented by the authors for acid slags can also be linearized in the coordinates N_{VO}/a_V vs a_{FeO} which indicates the possibility of the divalent vanadium significant amount presence in acid slags. When normalizing to pure solid VO, its activity coefficient was 0.42 and 0.31 at 1873 and 1923 K, respectively.

The investigation of the vanadium valence state and the activity of its oxides in slag melts was carried out by the authors [7]. Two groups of experiments were performed in a furnace with a controlled atmosphere: with pure slags of the CaO–SiO₂–Al₂O₃–V₂O₅ system and these slags in contact with iron-carbon melts of various compositions. The gas phase consisted of a various CO–CO₂ mixtures, equivalent to the partial oxygen pressure from $1.5 \cdot 10^{-6}$ to $2 \cdot 10^{-10}$ atm. The presence of two main vanadium valences was found: V⁵⁺ and V⁴⁺ at P_{O_2} more than 10^{-8} atm, V⁴⁺ and V³⁺ at P_{O_2} less than 10^{-8} atm. An increase in the CaO content promoted an increase in the share of vanadium with a higher valency. The results of the experiments could be affected by insufficient exposure time to achieve equilibrium and the oxidation of vanadium in the slag samples during sampling.

Experiments on the cathodic deposition of vanadium from oxide melts on solid electrodes showed [8] that, in the absence of a reducing agent and an air atmosphere, slag contain mainly V⁴⁺ form. In the atmosphere (CO+N₂) the V³⁺ form is stable. Pentavalent vanadium in the slag is unstable and goes into lower valence states. Upon contact with a carbon-saturated molten iron, vanadium is stable in the trivalent state. In a reducing atmosphere in the presence of solid vanadium, the main vanadium form in the slag is V²⁺.

The presence of vanadium in the metal melt probably provides a disproportionation reaction at the phase boundary



An X-ray diffraction study of the oxide films formed during oxidation on the metal surface showed that at a vanadium concentration in the metal of less than 0.2% vanadium spinel of variable composition is formed. V₂O₃ is formed in the range from 0.2 to 0.3% V. At V > 0.3%, the product of vanadium oxidation, according to the authors of [9], should be V₂O₂ oxide. A slightly different concentration range V was found in [10]. According to these data, V₂O₂ appears at V > 0.9%. There is an opinion [11,12] that in the Fe–V–O system at low temperature only FeO–VO solutions of variable composition can be in equilibrium with the metal melt. A similar point of view is shared by the authors of [13, 14]. The given point of view is based on studies of the products of iron deoxidation by vanadium. However, according to the review [15], depending on the O/V ratio in the metal, the products of deoxidation are V₂O₅ (V < 0.1–0.2%), V₂O₃ (with V contents from 0.15–1.8 to 10%) and VO (from 0.3–4 to 10% V in the metal).

The presence in iron of such strong reducing agents as carbon and silicon leads to the reduction of transition metal ions in oxide melts, especially with a high SiO₂ content, to a divalent state [16]. This vanadium valence state is confirmed by laboratory data on the smelting of vanadium-containing cast iron. Figure 1 shows that the equilibrium between the metal and vanadium slag is well described by reaction



Thus, there is still no clear insight of how various technological parameters affect the form of vanadium in the slag, which makes it difficult to select the optimal process conditions by calculation.

2. Calculation design

The polymer model [17] makes it possible to estimate the effect of slag composition on the distribution of vanadium by valency. We assume that tetravalent vanadium is present in the melt in the form of the VO²⁺ cation, and pentavalent is in the form of the VO₄³⁻ anion [18].

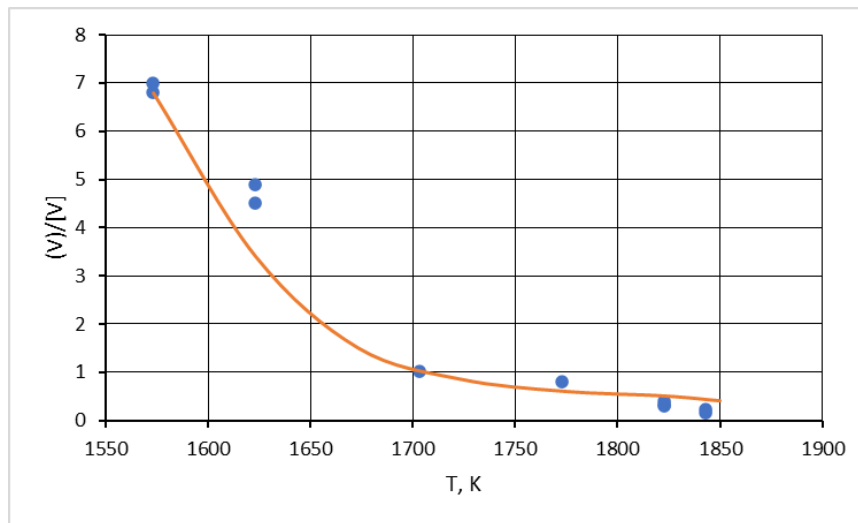
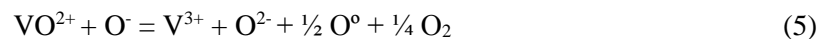
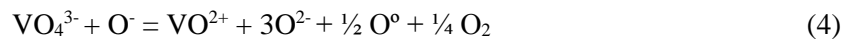


Figure 1. Vanadium distribution between slag and pig iron. Points are experimental values. Curve – calculation values for reaction (3).

Then the redistribution of vanadium valencies in oxide melts can be described by the equations:



Here O^- is the non-bridging oxygen ion, O^{2-} is the free oxygen of the slag, O^0 is the bridging oxygen atom. The suggested record takes account of the dependence of the vanadium valence forms on the partial pressure of oxygen and the oxide melt composition. The relationship between the various forms of oxygen in the slag is determined by the reaction



The model makes it possible to determine the ionic fractions of oxygen various forms in slags of various compositions and use them in the calculation. From equations (4)–(6) it follows that

$$\frac{a_{\text{VO}^{2+}}}{a_{\text{VO}_4^{3-}}} = K_4 \frac{a_{\text{O}^-}}{a_{\text{O}^0}^{1/2} \cdot p_{\text{O}_2}^{1/4}} \quad (8)$$

$$\frac{a_{\text{V}^{3+}}}{a_{\text{VO}^{2+}}} = K_5 \frac{a_{\text{O}^-}}{a_{\text{O}^{2-}} \cdot a_{\text{O}^0}^{1/2} \cdot p_{\text{O}_2}^{1/4}} \quad (9)$$

$$\frac{a_{\text{V}^{2+}}}{a_{\text{V}^{3+}}} = K_6 \frac{a_{\text{O}^-}}{a_{\text{O}^0}^{1/2} \cdot p_{\text{O}_2}^{1/4}} \quad (10)$$

The equilibrium constants K_4 – K_6 were found by combining the polymerization constant of reaction 7 and the equilibrium constants of reactions



K_{11} – K_{13} values were calculated from reference data [19]. Due to the absence of reliable data on the vanadium activity coefficients in slags, we equate its activity to mole fractions. Let us assume by convention that in the vanadium subsystem

$$N_{V^{5+}} + N_{V^{4+}} + N_{V^{3+}} + N_{V^{2+}} = 1 \quad (14)$$

Solving equations (8)–(10) and (14) simultaneously, can be found the fractions of all vanadium valence forms depending on the slag composition and the gas phase oxidative potential.

3. Calculation results

Figure 2 shows the results of the calculations for slag of the CaO–SiO₂ system at 1600 °C. It was believed that the concentration of vanadium oxides in the slag is deficient to affect the distribution of oxygen in three forms.

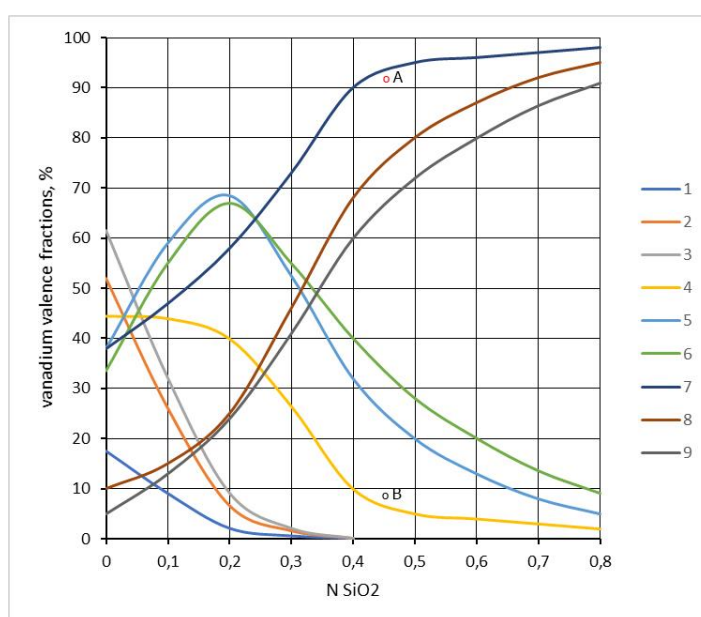


Figure 2. Dependence of the fractions of penta- (1–3), tetra- (4–6) and trivalent (7–9) vanadium on the SiO₂ content in the CaO – SiO₂ melt at a temperature of 1600 °C and an oxygen partial pressure of 0.001 (1,4,7), 0.21 (2,5,8) and 1.0 atm (3,6,9).

It can be seen that in silicate melts of the CaO–SiO₂ system, the main forms of vanadium are trivalent and tetravalent. Appreciable fractions of 5-valent vanadium are present with a molar fraction of SiO₂ of less than 0.3. The fraction of divalent vanadium even at $P_{O_2} = 0.001$ atm. varies from 0.066 to $7.75 \cdot 10^{-4}$ % and at P_{O_2} equal 1 atm. it is $3.20 \cdot 10^{-3}$ – $6.49 \cdot 10^{-5}$ %. The fraction of tetravalent vanadium changes through a maximum at the level of 50–70 %, the position of which in the diagram depends on the partial oxygen pressure. In slags with a basicity of 0.93 or lower, the largest fraction is V³⁺. The stable existence of trivalent and tetravalent vanadium at very close concentrations to the calculated values was confirmed experimentally for an argon atmosphere with an oxygen impurity of 0.001 atm. (points A and B).

To extend the proposed approach to other oxide systems, we evaluated the effect of the free oxygen concentration in the slag on the vanadium valence forms. This parameter can be obtained using the polymer model for most metallurgical systems for which polymerization constants are known. In addition, the authors of [20] suggested using the common logarithm of a ratio of the free oxygen ionic fraction to the polymerization constant as an indicator of the slag basicity. The authors have shown

that this indicator plays the same role as pH in aqueous solutions. The dependence of vanadium fractions on the basicity index in the air atmosphere is shown in Figure 3.

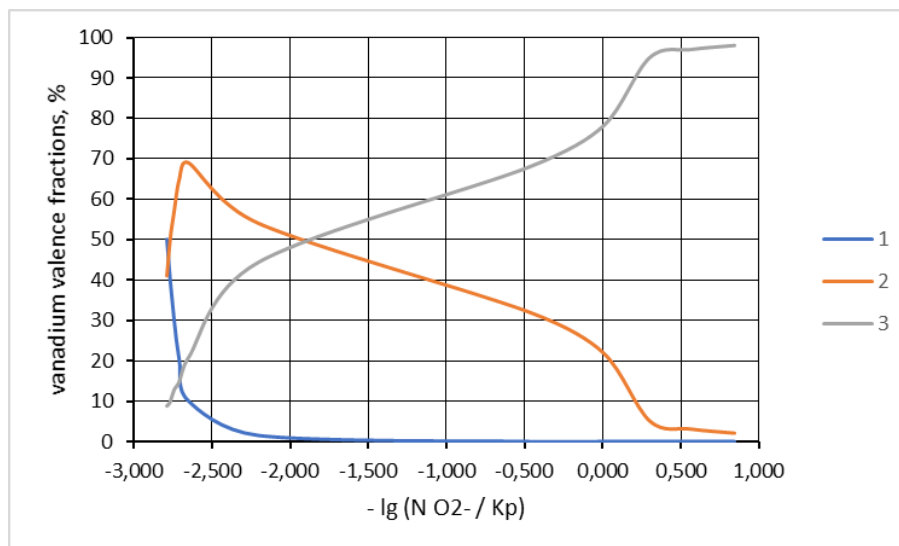


Figure 3. The dependence of vanadium valence fractions on the basicity index. Penta- (1), tetra- (2) and trivalent (3) vanadium.

Realization of similar calculations using metallic iron and FeO as reagents showed (Figure 4) that pentavalent vanadium practically disappears in the slag contacted with molten iron in the air atmosphere, and tetravalent fraction is greatly reduced. At the same time, a considerable amount of divalent vanadium appears, which increases with a decrease in basicity.

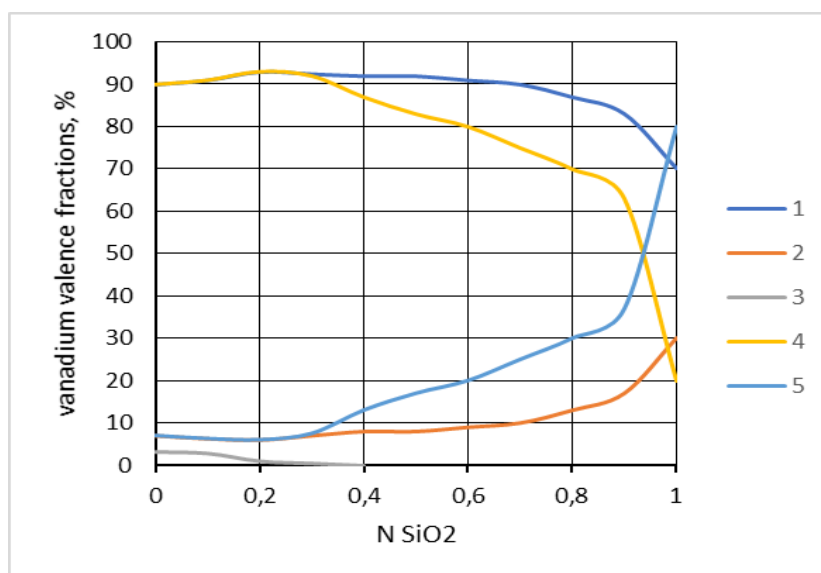


Figure 4. Vanadium valence forms in systems Fe–CaO–SiO₂ (1, 2, 3) and Fe–FeO–SiO₂ (3,4,5) at 1600 °C in air. 1,4 – V³⁺; 2, 5 – V²⁺; 3 – V⁴⁺.

Upon contact with the molten pig iron, as was shown earlier (see Figure 1), the divalent form of vanadium, apparently, becomes predominant.

The results do not contradict the data on the oxidation state of vanadium obtained by X-ray spectroscopy and High-Temperature Mass Spectrometry [21–25].

4. Conclusions

Thus, the polymer model provides an effective estimate tool for the prevailing vanadium valence forms in slags depending on the process conditions. In particular, using the polymer model, the influence of the slag composition and the gas phase oxidation potential on the distribution of vanadium oxidation state is shown.

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